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SEMICONDUCTING OXIDE GLASSES

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J. D. Mackenzie

I. INTRODUCTION

The electrical properties of oxide glasses have been extensively studied for over a hundred years. Most of the systems that have been examined, such as the soda-lime-silicate glasses, for instance, all contained high concentrations of alkali oxides. It is well established that for such glasses, from room temperature to the softening points, the mechanism of electrical conduction is electrolytic or ionic, the principal charge carriers being the alkali ions present.¹ For these materials, it has been conclusively demonstrated that Faraday's Laws are obeyed and the transport number of the alkali ions present, for instance Na^+ , is unity.¹ The deterioration or polarization of common silicate glasses under a DC potential is of course well known. Such experimental evidence has led to statements in many authoritative texts on glass that all oxide glasses are ionic conductors. The correct statement should perhaps be "most known oxide glasses are ionic conductors".

Oxide glasses in which electrical conduction is electronic in nature are not widely known. In this chapter we will first endeavor to answer the question: "Can oxide glasses be theoretically expected to exhibit bulk electronic conduction?" Available experimental results on the electrical properties of oxide glasses which have been reported to be electronic conductors will then be reviewed.

II. DEFINITION OF SEMICONDUCTING OXIDE GLASS

The term "electronically conducting glass" has frequently been applied to surface conduction of oxide glasses. It is well known, for instance, that a lead-containing glass can be reduced in hydrogen to give a thin surface layer of metallic lead.² Alternately, a transparent layer of a semiconductive oxide such as SnO_2 can be deposited on a glass substrate.³ For these materials, the electrical conductivity which is of interest is that of the surface layer. The bulk resistivity of the glass substrate remains high and the conduction mechanism remains ionic. The present chapter is not concerned with such surface conducting materials, but rather with bulk or volumetric electronic transport inherent to the glass network itself.

For all oxide glasses in which bulk electronic conduction has been reported, the resistivity invariably decreases with increasing temperature. Thus in order to minimize confusion

with metallic conduction, the temperature coefficient of which is of different sign, and also with surface-conducting glasses, the word "semiconducting" is considered preferable to "electronically conducting". A semiconducting glass is presently defined as a homogeneous, single-phased, and non-crystalline solid in which (a) bulk electrical conduction at the temperature in question occurs predominantly by electrons (and/or holes) rather than by ions, and (b) the temperature coefficient of resistivity is negative.

III. BULK ELECTRONIC CONDUCTION IN GLASS

Since experimental and theoretical studies of semiconductors, oxides or otherwise, have hitherto been confined to crystalline materials, the concept of a semiconducting oxide glass may not be readily acceptable. Indeed, with the wealth of experimental data that most known oxide glasses are ionic conductors, the question may be raised if an oxide glass can actually exhibit semiconduction. The answer is immediately obvious if we regard a glass as a "rigid liquid" since many liquid electronic conductors are known. A detailed review on many liquid systems has been prepared by Ioffe and Regel,⁴ and therefore only a brief outline is given here.

That long-range order is not a prerequisite for metallic

conduction is easily demonstrated from the observed electrical properties of liquid metals.⁴ The fusion of many crystalline semiconducting oxides such as V_2O_5 , FeO , and CoO also gives melts which are semiconducting.^{4,5} Thus, for V_2O_5 , a n-type semiconductor, the electrical conductivity increases gradually when the crystal is heated and no sharp variation is observed when melting occurs.⁶ This behavior is shown in Figure 1 in which the large variation of conductivity on melting for a typical ionic oxide, PbO , is included for comparison. Crystalline FeO , for instance, is known to be a p-type semiconductor deficient in iron. Again there is no marked change of conductance on fusion.⁷ Similar to the case of V_2O_5 , the temperature coefficient of resistivity of the crystal remains negative on melting and electrolysis is not observed under a DC potential. The ionic transport numbers of molten CoO , NiO and Cu_2O are⁸ estimated to be less than 10^{-3} . It appears certain then that long-range order is also not a prerequisite for electronic conduction in semiconducting oxides. From a priori reasoning, therefore, it would seem probable that if oxides such as V_2O_5 and FeO can be prepared in the vitreous state, then their mechanisms of electrical conduction should be electronic rather than ionic. Unfortunately, these transition metal oxides are not easily obtainable in the glassy form by conventional methods

such as quenching of the melt. There is therefore little available experimental data to support the above hypothesis. Preliminary work by the present author⁹ on glassy V_2O_5 films, formed by vapor deposition, has shown, however, that the conduction mechanism is indeed electronic in nature.

IV. GENERAL PRINCIPLE FOR THE PREPARATION OF SEMICONDUCTING GLASS

Since the transition metal oxides by themselves, for instance, pure V_2O_5 or FeO , are not easily rendered into the vitreous state, our attention must be focused on polycomponent systems involving other oxides. Such systems should preferably give a homogeneous melt which can be easily supercooled to give a rigid glass. A semiconducting oxide may, for instance, be fused with a "network former" such as SiO_2 or P_2O_5 , with or without a "modifier" like Na_2O or CaO to give a glass. For such a polycomponent system it is obvious that if the glass is required to be a semiconductor at any temperature, the mobility of the ions in the system must be negligibly small. Recently it has been shown that at all temperatures below the glass transition region, the mobility of divalent ions, such as Ca^{++} and Sr^{++} and other metal ions of higher valence, is extremely low for all types of oxide glasses.¹⁰ Further, these immobile polyvalent ions in the glass network can impede the motion of any alkali ions which may be the normal current carriers. Depending on composition, the ionic

conductivity of such an oxide glass containing as much as 15 mole % Na_2O can be negligible at room temperature. In Figure 2, the electrical resistivity of some silicate and borate glasses of relatively high sodium concentration is seen to be greater than that of a sample of fused silica of lower sodium content. These systems can therefore be considered as "high-resistivity" bodies and thus suitable as a constituent for the preparation of semiconducting oxide glasses.

If a glass is indeed readily prepared from a melt containing, say, B_2O_3 , (the glass-former) CaO and Na_2O (the modifiers), and a high concentration of V_2O_5 (the semiconductor), the second question will necessarily be on the behavior of the V_2O_5 constituent. Or, rather, the behavior of the vanadium ions in the resultant glass. A qualitative indication is available from a consideration of the properties of the crystalline oxide itself. For the crystalline oxide semiconductors such as V_2O_5 , Fe_2O_3 and NiO , the mobility of the carriers is extremely small. This may be $10^{-2} \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ as compared to values of $10^3 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ or more for elemental semiconductors like germanium.⁴ The mean free path of the carriers in these semiconducting oxides, either electrons or positive holes, calculated from such low mobilities, can be less than the interatomic distances in question. Ioffe and Regel⁴ have depicted this as the fading out of electron waves

within the limits of a single unit of the crystal lattice.

The motion of the carrier between ion cores is thus described as a "hopping: or "jumping" process. For an iron oxide, for example, this can be formally represented by:



The motion of the electron from Fe^{2+} to Fe^{3+} is apparently not impeded by the relatively large distance of separation of these ions nor by the presence of oxygens around them.¹¹

It has already been demonstrated that long-range order is not the only criterion for semiconduction (Figure 1). Secondly, it is known that the transfer of electrons or holes between metal ion cores which are separated by oxygens is possible. Thirdly, the mobility of divalent and higher valence ions such as Ca^{2+} and Al^{3+} is extremely small in solid glasses and their presence apparently also impedes the motion of alkali ions in the system. A general principle for the preparation of semiconductivity oxide glasses is now apparent from a combination of these facts. Based on this broad principle, the present author has prepared a large variety of semiconducting glasses.¹² For instance, a "high resistivity" glass described above may be used as an inert matrix into which a large amount of one or more semiconducting oxides are incorporated. That is, a semiconducting glass can be regarded as the concentrated solution of an

electronic conductor in an insulating glassy solvent. Some of these systems are described below.

It is recalled that because of the lack of data on the polycomponent solid glasses and the difficulty of preparing a one-oxide semiconductive glass such as V_2O_5 or Fe_2O_3 , the above hypothesis was based partially on the observed electrical properties of melts. It is pertinent to mention that anomalous behavior has been observed in the melts of various systems when the liquid is composed of a "network-former" and a semiconducting oxide. Thus for melts of the system $FeO-SiO_2$, the ionic transport number at $1400^\circ C$ is less than 0.1 from pure FeO to about 88 mole % FeO . The ionic transport number increases rapidly thereafter until it is greater than 0.9 at 62 mole % FeO ¹³. Similar behavior was observed in the system $CoO-SiO_2$ ¹⁴. It is interesting to note that the ionic transport number actually increases when the fluidity of the melt decreases. An obvious qualitative explanation is that the structure of the melt changes fairly rapidly when an appreciable amount of SiO_2 is present to affect the electronic conduction mechanism. Detailed experimental and theoretical studies, however, have not been carried out.

V. EXPERIMENTAL VERIFICATION OF ELECTRONIC CONDUCTION

Most of the semiconducting oxide glasses described in the literature are based on the system $V_2O_5-P_2O_5$. Although such

glasses were first prepared in 1867 by Roscoe²⁹, the early workers were apparently not interested in the electrical properties. Thus Tammann and Jenckel³⁰ studied the effects of pressure on the density of V_2O_5 - P_2O_5 glasses and not their electrical properties. Denton, Rawson and Stanworth²¹ were the first to suggest that these vanadate glasses are n-type semiconductors. Since 1954, a variety of other semiconducting oxide glasses has been reported. These are summarized in Table I. In most of these studies, no description is even given of a) any proof that the conduction mechanism is truly electronic and not ionic and b) any critical examination that the observed electronic conductivity is not due to one or more crystalline phases present in the glass. In this section, those few studies in which an experimental verification of electronic conduction has been carried out will be reviewed.

a) Electrolysis

In general, an ionically conducting oxide glass will exhibit polarization phenomena in a DC field. Thus the electrical resistance of a sample at a constant temperature will increase with time. Baynton, Rawson and Stanworth¹⁵, for instance, stated that the resistance of V_2O_5 - P_2O_5 -BaO glasses is not time-dependent. No details are given, however, on the tests. It must be emphasized that a single observation that the resistance

is constant with time does not constitute sufficient proof that the conduction mechanism is totally electronic in nature. Thus the applied voltage, the resistance of the sample, and the duration of the application of the DC field, all have to be taken into consideration.

The effects of 200-volt DC on a number of ionically conductive and semiconducting glasses studied by the present author are shown in Figure 3. The resistances of the three ionically conducting samples, namely, fused silica, a microscope slide, and a Corning No. 0080 soda-lime silicate, all increased with time. The others, presumably all semiconducting glasses, show no time-dependency of electrical resistance. In fact, the resistances of some samples are constant at 10^6 ohms after 48 hours under a 200 volt DC potential.¹²

When the resistance, voltage, time and sample areas are known, the predominance of electronic conductance can also be demonstrated by another method. For instance, in one of the glasses shown in Figure 3 having the composition of 30 mole % CoO, 47 mole % B₂O₃, and 23 mole % CaO, the concentration of Co⁺⁺ ions is approximately 0.26 gm per cc. The composition can be represented simply as 3CoO.2.3 [2B₂O₃.CaO]; that is, as a mixture of CoO and a calcium borate glass of the composition CaO.2B₂O₃. At 350°C, the electrical resistivity of the glass CaO.2B₂O₃ is about 10^{12} ohm-cm. The addition of the CoO is

apparently effective in reducing the resistivity to below 10^7 ohm-cm at 350°C . If the conductivity is ionic in character, then either Co^{++} and/or O^{--} ions may be the principal current carriers. Under a DC potential, electrolysis must occur. The amount of Co^{++} ions deposited in the cathode is given by:

$$W = Itq / F \quad (1)$$

where I is the current, t is the time, q is the equivalent weight and F is the Faraday. For a sample having a resistance of 10^6 ohms at 200 volts DC, W is 2×10^{-3} gm after 10 hours. Now the electrode area is about 1 cm^2 and therefore a layer of glass adjacent to the anode, approximately 0.1 mm thick, will be depleted of Co^{++} . Thus after 10 hours, the resistance of the resultant glass should be:

$$r = r_i + r_o \quad (2)$$

where r_i is the resistance of that major portion of the glass sample containing the initial amount of Co^{++} (i.e., 30 mole % CoO), and r_o is the resistance of the thin layer containing no Co^{++} ions (i.e., a glass of the composition $\text{CaO} \cdot 2\text{B}_2\text{O}_3$). It is estimated that r_o is about 10^{11} ohms. Thus r must be at least 10^{11} ohms after 10 hours. However, the initial resistance of 10^6 ohms has not increased at all after 16 hours. There is thus little doubt that the conduction mechanism in this glass containing CoO is electronic rather than ionic.

In another example, Mazurin and co-workers²⁵ studied a glass of the composition $\text{Fe}_2\text{O}_3 \cdot 3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot 4\text{SiO}_2$. Transport measurements were carried out at 580 to 650°C using a Hittorf-type cell with different electrode materials. The maximum observed weight change in a sample at 650° was about 5% of the calculated value for Fe^{3+} ionic conduction. In another sample at 580°, the observed weight change was only 0.3% of the estimated value. The authors therefore concluded that the conductivity was purely electronic.

b) Measurement of Electromotive Force

An oxide glass containing mobile ions may be considered as a solid electrolyte. The transport number of the ions can be obtained by using the glass as the electrolyte in a galvanic cell. The theory has been discussed in detail by Wagner³¹ and successful use of such a technique to obtain the ionic transport number of crystalline oxides is exemplified by the work of Mitoff.³² If the two ends of a glass sample at any temperature T are in contact with atmospheres of different partial pressures of oxygen p_1 and p_2 , then for a pure ionic or electrolytic conductor, the theoretical emf is given by:

$$E_t = \frac{2.3RT}{4F} \log(p_1/p_2) \quad (3)$$

where R is the gas constant and F is the Faraday. For a mixed ionic-electronic conductor, the ionic transport number is simply

$$t_i = E_o / E_x, \quad (4)$$

where E_o is the observed emf of the cell. For a pure electronic conductor, E_o is zero.

An apparatus used by the present author¹² for a study of semiconducting glasses is shown in Figure 4. The glass samples were approximately 1 mm thick discs of diameter 1 to 2 cm. Different partial pressures of oxygen were obtained by the use of CO_2 , O_2 and air atmospheres. When typically ionic glasses such as the Corning No. 0080 were tested, the technique was disappointing in that only qualitative measurements could be made. Invariably, instantaneous polarization was encountered and E_o seldom remained constant with time. Qualitatively, however, E_o was always large and corresponded approximately to the appropriate values of E_t . For a "0080" glass, for example, if CO_2 and O_2 are the two gases in contact with the opposite faces of the sample, E_t is approximately 0.1 volt. For the semiconducting glasses shown in Figure 3, E_o was always less than 10^{-3} volt. Within the limits of experimental error, therefore, it could be concluded that these glasses were predominantly electronic conductors.

c) Magnitude of Electrical Resistivity and Activation Energy.

For both ionically conducting and semiconducting oxide glasses, the temperature coefficient of electrical resistivity is negative. Over a limited temperature range, resistivity is

usually described by the Arrhenius equation:

$$\rho = \rho_0 \exp(E^*/RT) \quad (5)$$

where ρ_0 is a constant and E^* is the so-called activation energy for conduction. The magnitude of either ρ or E^* by itself is not always indicative of the mechanism of conduction. However, the comparison of ρ and E^* of glasses with and without the semiconducting component can be instructive. Alternately, a study of ρ and E^* as a function of the composition of a system which can exhibit both ionic and electronic conduction is also enlightening.

In Table II, some semiconducting systems are shown, of which the activation energies for electrical conduction have been evaluated by the present writer.¹² In sample No.1, for example, E^* refers to the glass of the composition shown. E^1 is the activation energy for conduction of a glass having the composition 60 mole % GeO_2 and 40 mole % BaO . In samples 2 and 3, E^1 refers to glasses of the composition 40 mole % CaO and 60 mole % B_2O_3 . In all three cases, E^1 is greater than E^* . Now, if V^{5+} , Fe^{3+} and Co^{2+} ions are the current carriers, then E^* is expected to be greater than, or at most equal to, E^1 . The fact that E^* is actually much less than E^1 is indicative that these glasses are not ionic conductors.

In Section V a) above, it was mentioned that at 350°C the

electrical resistivity of a glass of the composition $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ was about 10^{12} ohm-cm. The addition of a substantial amount of CoO was effective in reducing the resistivity to about 10^6 ohm-cm. Now the electrical resistivity for an ionically conducting system is approximately related to the so-called ion-oxygen attraction given by:

$$I = \frac{z_1 z_2 e^2}{d^2} \quad (6)$$

where z_1 and z_2 are the valences of the oxygen and cation respectively and d is the inter-ionic separation, and e is the electronic charge. The ionic radii of the Co^{2+} and Ca^{2+} ions are 0.73Å and 0.99Å respectively. The ion-oxygen attraction for Co-O is 25% greater than that for Ca-O . If the cobalt-containing glass is ionically conducting, then the resistivity should be higher than that with the calcium but no cobalt. However, not only was the opposite result found, but the resistivity had decreased from 10^{12} ohm-cm to 10^6 ohm-cm when CoO was present. Such considerations are again fairly clearly indicative of electronic conduction.

The studies of Evstrop'yev and Tsekhonskiy²⁶ on the system $10\text{Fe}_2\text{O}_3 \cdot 20\text{CaO} \cdot 10\text{B}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3 \cdot 55\text{SiO}_2$ (in mole %) were convincing that the glass was a semiconductor. These workers replaced the SiO_2 partially with Na_2O and measured both the electrical conductivity as well as the diffusion coefficient of the sodium. It was found that up to 5% Na_2O while the diffusion coefficient

of the sodium had increased by two orders of magnitude, the conductivity was unchanged. Secondly, the activation energy for sodium diffusion varied from 103 to 85 kcal/mole while that for conductivity was constant at 31.2 kcal/mole. A third indication that the conduction was not ionic was obtained from the Nernst-Einstein relationship:

$$D/\sigma = \alpha kT / Ne^2 F^2 \quad (7)$$

where D is the ionic diffusion coefficient, σ is the specific conductivity, k is Boltzmann's constant, T is the absolute temperature, N is the number of current carriers per cc, e is the electronic charge, and F is the Faraday. For most ionically conducting glasses, α , the correlation factor, is between 0.3 and 1.0. For the glasses examined by Evstrop'yev and Tsekhomskiy,²⁶ α varied from 0.001 to 0.02 when as much as 3 mole % Na₂O was present. Similar glasses containing no iron oxide gave α values of 0.6 ± 0.2 .

Grechanik and co-workers²⁸ studied a base glass of the composition 40 PbO.60 SiO₂ (in mole %). In one series of experiments, the PbO was replaced by Fe₂O₃; in another, PbO was replaced by Na₂O. Both the resistivity and the activation energy of the iron-containing glasses were appreciably less than those for the sodium-containing glasses of comparable composition. These authors also concluded that the iron-containing glasses

were not ionic conductors.

The electrical resistivity data on a large number of complex silicate glasses containing transition metal oxides such as FeO and MnO were treated somewhat differently by Trap and Stevels³³ to show that these were electronic conductors. These authors showed that in general, the electrical resistivity of all the glasses was represented by the empirical relations:

$$\log \rho = A + B/T \quad (8)$$

and $A = \underline{m}Q + \underline{n} \quad (9)$

where A, B, m, n, are constants, and Q is the activation energy for conduction. For glasses containing none or small amounts of transition metal oxides, \underline{m} varied from -5 to -9 and \underline{n} from 2 to 10. However, when the Fe₃O₄ content was in excess of 18 mole %, say, \underline{m} was +32 and \underline{n} became -0.1. Further, in the glasses with relatively high concentrations of transition metal oxides, Q varied from 0.03 to 0.10 e.v. When the amounts of oxides such as Fe₃O₄ and MnO were decreased to a critical amount, depending on the particular glass, Q jumped abruptly to 0.6, to 0.9 e.v. The resistivities of the glasses with high concentration of transition metal oxides also showed no pronounced changes on the continued flow of direct current. It was therefore concluded that these were indeed semiconducting glasses.

d) Effect of Pressure on Conductivity

As a first approximation, the structure of oxide glasses

may be regarded as a network of oxygen ions linked together tightly by the smaller "glass-forming" ions such as silicon and boron. Larger cations like Na^+ or Ca^{++} are held relatively loosely in the interstices of the network. Ionic conduction may be regarded as the motion of the cations through the "holes" of the network. This would suggest that conductivity is directly related to the specific volume of the glass. Littleton and Wetmore,³⁴ for instance, showed that the resistivity of chilled samples of silicate glasses (larger specific volume) was less than that of well-annealed samples. For a typical ionic conductor such as crystalline AgBr, the resistivity, as expected, increases with increasing hydrostatic pressure.³⁵ The writer is unaware of any experiments in which the resistivity of an ionically-conducting solid actually behaves anomalously; that is, decreases with increasing pressure. On the other hand, the resistivity of semiconductors, for instance, InSb and GaSb,³⁶ or the transition metal oxides,^{37,38} may decrease or increase with increasing pressure.

In Figure 5, the effects of pressure on the resistivity of two samples of $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ glasses are shown for two different temperatures. In both cases, the pressure coefficient of resistivity is seen to be negative. This, together with the results of electrolysis experiments, are fairly conclusive evidence that these glasses are not ionic conductors.

VI. ELECTRICAL CONDUCTIVITY

At present there is no quantitative, or perhaps even semi-quantitative, theory on electrical conduction in semiconducting oxide glasses. Following the limited work on crystalline transition metal oxides such as NiO, various authors^{16,19} have suggested that a similar mechanism must be operative in the non-crystalline material. Thus conduction is pictured to be the transfer of an electron (and/or hole) between ions of the same transition metal in different valence states. In a V₂O₅ containing glass, for instance, the motion of an electron can be represented by:



From the considerations given in the previous sections, it is evident that qualitatively, the electronic conductivity will be governed by many factors which include:

- a) Concentration of the transition metal oxides.
- b) Ratio of the high/low valence ions; e.g., V^{5+}/V^{4+} , Fe^{3+}/Fe^{2+} , etc.
- c) Magnitude of the contribution of ionic conductivity. For instance, a glass may be a mixed electronic/ionic conductor.
- d) Average separation distance of the transition metal ions. For instance, the same molar concentration of V₂O₅ in a borate or a silicate glass may give different average separation of the vanadium. Since metal oxides such as Na₂O and PbO may interact differently with the glass-former, some effects are also to be expected from them.

From an experimental point of view, the problem is further

complicated by the additional factors:

- e) Thermal history. It has been shown that the annealing temperature and the time can have a large effect on the magnitude of the conductivity of a semiconducting glass.²³ The melting temperature of a V_2O_5 - P_2O_5 - RO glass influences the V^{4+}/V^{5+} ratio and thus also affects the conductivity.¹⁶
- f) Identification of ionic species. It is often difficult to identify the ionic species and unambiguously estimate the high/low valence ratio.
- g) Atmosphere. Since conductivity is dependent on the high/low valence ratio, the ambient atmosphere during measurement, especially at high temperatures, is an important consideration.

A critical examination of the published conductivity results has revealed that in most cases, the authors have failed to mention or control one or more of the above factors. Much of the available data are thus of little value for quantitative evaluation. Despite the large amount of work on the system V_2O_5 - P_2O_5 - BaO , for instance, there is still only disagreement between different workers and little understanding of the nature of the conduction. This criticism will become evident in (2) below.

1. General Conductivity Results

Published results (see Table I) showed that the electrical conductivity of all semiconducting glasses increased with increasing temperature according to eq.(5). Some typical results

on the V_2O_5 - P_2O_5 -RO glasses obtained by Baynton et al.¹⁵ are shown in Figure 6. The results of some other types of semi-conducting glass based on the present author's work are shown in Figure 7.

In general, the conductivity is directly proportional to the concentration of the transition metal oxide present. This is illustrated by the results on the binary system V_2O_5 - P_2O_5 in Figure 8. It must be emphasized that in all the results shown in Figure 8 the values of the V^{4+}/V^{5+} ratio are unknown.

In the qualitative model for conduction described above, electronic conduction will be unlikely if all the transition metal ions are in the same valence state. In general, then, when the concentration of one ionic species far exceeds the other, conductivity should be proportional to the ratio of the concentration of the two ions. The results obtained by the present author⁹ on a glass of the composition $CaO.2B_2O_3$ containing Fe_3O_4 are shown in Figure 9. It is evident that the resistivity was changed when the Fe^{2+}/Fe^{3+} ratio was altered.

The lowest resistivity so far obtained for the semiconducting oxide glasses is approximately 10^3 ohm-cm at 25°C. A number of V_2O_5 - P_2O_5 -RO glasses containing high concentrations of V_2O_5 (greater than 80 mole %, say), can exhibit such low resistivity.^{15,23} Although lower resistivities, about 10 ohm-cm at 25°C, have been reported on complex glasses containing more than 30 mole % iron

³³
oxide, it is not clear if crystalline phases present are responsible for the observed conductivity.

2. Glasses Based on V_2O_5 - P_2O_5 -RO

Most of the published work are on glasses based on V_2O_5 - P_2O_5 with or without other metal oxides. This is presumably because of the low melting temperatures and the relative ease of glass formation. In general, agreement between the conductivity results of different workers is poor. For the glass $60V_2O_5$ - $20P_2O_5$ - $20BaO$ (in mole %), for instance, the resistivity at $40^\circ C$ is 4×10^5 ohm-cm according to Munakata.¹⁶ Grechanik,¹⁷ however, reported a value of 2×10^7 ohm-cm. In the absence of information on the appropriate factors governing conduction as described above, it is impossible to assess the nature of such controversy. Some of the results from the studies of Baynton et al.¹⁵ are shown in Figure 6. The activation energies for conduction, E^* of eq. (5), are surprisingly constant in the systems V_2O_5 - P_2O_5 - BaO , V_2O_5 - P_2O_5 - Na_2O and their mixtures over wide ranges of composition. Thus E^* ranges from 0.34 to 0.39 e.v. when V_2O_5 varies from 87.5 to 50.8 mole %, P_2O_5 from 10 to 30 mole %, BaO from 2.3 to 20 mole %, and Na_2O from 6.5 to 10.8 mole %. Apparently, the ionic contribution to electrical conductivity is still negligible even when 10.8 mole % Na_2O is present in these glasses.

There is wide disagreement between both the observed results and the interpretation of different workers for glasses of this group. Baynton et al.¹⁵, for instance, showed that when the V_2O_5 content is similar, glasses in the system V_2O_5 - P_2O_5 -BaO system have higher resistivities than those in the system V_2O_5 P_2O_5 -BaO - Na_2O . It was considered that Na_2O was effective in increasing the electronic conductivity. Ioffe et al.¹⁹, however, maintained that the ratio V_2O_5/P_2O_5 is the only important factor governing the conductivity. The sodium and barium are considered as "fillers" in the holes of the glass network and have no effect on the conductivity. The results of Baynton were replotted by Ioffe et al. and seemingly support this idea as shown in curve (2) of Figure 10. Indeed all the room temperature results of Baynton et al. on glasses with Na_2O and/or BaO seem to fall on curve (2). Interestingly, the results of Ioffe et al., and Kitaigorodskii and Karpechenko⁴⁰ on V_2O_5 - P_2O_5 and V_2O_5 - P_2O_5 -BaO are described by curve (1) of Figure 10. We have included the recent results of Hamblen and coworkers²³ for BaO and CdO containing glasses for comparison. It is evident that no conclusion can be drawn from such a plot.

That the ratio V_2O_5/P_2O_5 is indeed important is evident from the work of Nador⁴¹ who actually showed that when V_2O_5 and P_2O_5 were melted together in nitrogen, oxygen gas was evolved. The

amount of oxygen evolved was proportional to the amount of P_2O_5 in the melt. Nador attributed this to the reduction of V_2O_5 to V_2O_4 . Unfortunately, no mention was made of the time and temperature dependency of these experiments. Although Ioffe et al. did show the importance of the V_2O_5/P_2O_5 ratio, no estimate was given of the V^{5+}/V^{4+} ratio of their glasses.

Munakata¹⁶ showed that the difference in the conductivity at 40°C of glasses of the molar composition $60V_2O_5 \cdot (40-x)P_2O_5 \cdot xBaO$ which was caused by melting at 900°C and 1100°C was due to a dissimilar V^{4+}/V^{5+} ratio. When the V_2O_5 content was constant, the resistivity at 40°C was only dependent on the V^{4+}/V^{5+} ratio and not on the BaO/P_2O_5 ratio. The measurements were confined to one temperature, namely, 40°C, and again makes a detailed interpretation of the results difficult, if not impossible. The results for the BaO containing glass are reproduced in Figure 11. Similar plots, all containing a resistivity minimum, ρ_m , were obtained for twelve other oxides.²² The values for ρ_m were considered to be a function of the cationic field strength, Z/a^2 where Z is the charge of the cation and a is mean distance between oxygen and cation. Whether this relationship holds at any temperature other than 40°C is unknown. The values of ρ_m range from 7×10^4 ohm-cm for Tl^+ to 6×10^5 for Ca^{++} , and would seem to invalidate the argument of Ioffe et al.¹⁹ on the role

of cations in these glasses.

The effects of thermal history on the room temperature resistivity of $V_2O_5.P_2O_5.RO$ glasses were studied by Hamblen and co-workers.²³ The resistivity of a glass containing 75 wt. % V_2O_5 and 25 wt.% $Cd(PO_3)_2$ was 1×10^4 ohm-cm when freshly made by quenching. After heating at 310° for 5 hours and then cooled down, the resistivity has increased to 1.5×10^5 ohm-cm. On the other hand, the resistivity of a glass containing 75 wt.% V_2O_5 and 25 wt.% KPO_3 , after similar treatment, decreased from 2.4×10^5 ohm-cm to 21 ohm-cm. Although the authors reported that the glasses were still "vitreous" after the heat treatment, it is likely that some phase separation, either liquid-liquid or liquid-crystal, has occurred to give such unusual behavior.

Most authors have attributed the conductivity of $V_2O_5.P_2O_5.RO$ glasses to the transfer of charges between V^{4+} and V^{5+} ions. The chemical analysis of Kitaigorodskii and Frolov⁴² appeared to be satisfactory and is in support of the presence of V^{5+} and V^{4+} ions in the glass. From magnetic susceptibility measurements, Azarov ²⁰et al., however, suggested that in glasses of the system $V_2O_5.P_2O_5.Na_2O$, the predominant ionic species are the lower ions such as V^+ , V^{2+} and V^{3+} .

It is hoped that the above survey on the conductivity of

glasses of the $V_2O_5 \cdot P_2O_5 \cdot RO$ systems is sufficient to demonstrate the complexity, the wide disagreement, and the need for additional and careful experimental work in this area.

VII. THERMOELECTRIC POWER AND CONDUCTIVITY TYPE

Crystalline semiconducting metal oxides are known to exhibit both n-type and p-type conductivity. In general, this is caused by the departure from stoichiometry in one of the two directions. Crystalline FeO , for example, is an iron-deficient semiconductor. A small proportion of the iron ions are in the Fe^{3+} state. These minority ferric ions are deficient of an electron with respect to the surrounding Fe^{2+} ions and may therefore be regarded as sites for positive holes. Crystalline FeO is thus a p-type semiconductor. Conversely, crystalline V_2O_5 is deficient in oxygen and some of the vanadium ions are in the V^{4+} state. As expected, it is a n-type semiconductor.

If the short range order in a particular crystalline semiconducting metal oxide is unchanged when "dissolved" into a glassy matrix, for example, V_2O_5 in P_2O_5 , then we may expect the same conductivity type in the glass. Thus in a first approximation, both n-type and p-type semiconducting oxide glasses can be readily prepared.

Almost all the glasses based on V_2O_5 are n-type semiconductors

according to Baynton ¹⁵ et al., Munakata, ¹⁶ and Ioffe ¹⁹ et al. These authors only observed the sign (i.e., positive or negative) of the thermoelectric power without actually measuring the latter. Munakata ¹⁶ obtained the V^{4+}/V^{5+} ratio by chemical analysis and reported that vanadate glasses were still n-type semiconductors when the V^{4+} concentration reached 40% of the total vanadium present. Qualitative Hall effect measurements were carried out by Hamblen and co-workers, ²³ who confirmed that the vanadate glasses are n-type materials. No estimate of the V^{4+}/V^{5+} ratio in the glasses were reported. Apparently, the Hall coefficient was too small to permit accurate measurements.

The most interesting study on the V_2O_5 - P_2O_5 glasses was carried out by Kitaigorodskii and co-workers. ¹⁸ The P_2O_5 was kept constant at 20 wt.% (24 mole %) and the V^{4+}/V^{5+} ratio was varied by the addition of lamp-black to the melt. The variation of the thermoelectric power with V_2O_4 (i.e., V^{4+}) content is reproduced in Figure 12. The thermoelectric power is seen to become increasingly less negative with increasing V^{4+} content. (Negative thermoelectric power indicates predominantly n-type conduction). In another glass of the composition 38.9 P_2O_5 . 38.4 V_2O_4 . 22.7 V_2O_5 (in wt. %), a positive thermoelectric power was observed which indicated that the predominant carriers were now positive holes. Kitaigorodskii therefore concluded that the vanadate

glasses were mixed conductors; i.e., holes and electrons.

The effects of metal oxides on the thermoelectric power of V_2O_5 - P_2O_5 glasses were studied by Grechanik et al.¹⁷ The P_2O_5 content was fixed at 20 mole % and the ratio of V_2O_5/RO then varied. Some of these results are shown by the dashed curves in Figure 13. Attempts by the present writer⁹ to repeat the measurements resulted in the other points shown in Figure 13. Even if we assume that the sign convention of the thermoelectric power is different, there is still considerable difference between the two sets of data. It is evident that the metal oxide does have an effect on the thermoelectric power. Any other more detailed discussion must await the results of further experimental studies.

For glasses based on Se-S-As, the sign of the carriers indicated by thermoelectric measurements is sometimes opposite to that given by Hall effects.⁴³ This anomaly has been attributed to the presence of small amounts of other phases in the glass. C. J. Phillips has reported that in a study of V_2O_5 - TeO_2 glasses, thermoelectric measurements indicated n-type conduction, whereas Hall effects measurements gave the opposite answer.⁴⁴ Presumably inhomogeneity also existed in the glass.

Some high temperature glasses of the system $MnO \cdot Al_2O_3 \cdot SiO_2$ were examined by McMillan.²⁴ As expected, conduction was of the

p-type. McMillan attributed this to the presence of Mn^{3+} ions in a system in which Mn^{2+} ions predominated. No actual measurement of thermoelectric power was reported.

In general, the thermoelectric power of the $\text{V}_2\text{O}_5\cdot\text{P}_2\text{O}_5\cdot\text{RO}$ glasses does not have a high temperature coefficient. Grechanik et al.¹⁷ reported that it was practically independent of temperature between 20° and 200°C. Some of the results obtained by the writer are shown in Figure 14. The words lead, alumel, and chromel refer to the reference metal from which the thermo e.m.f. was obtained. It is seen that the thermo e.m.f.s are indeed not very sensitive to temperature.

VIII. POSSIBLE APPLICATIONS

Since semiconducting glasses are of fairly recent origin and the accurate control of their electrical properties is governed by a large number of interdependent factors, no practical applications have been reported so far. It is obvious that in any usage whereby the ready polarization of conventional soda-lime type glasses is undesirable, a semiconducting glass will be preferable. McMillan²⁴ has indicated that the semiconducting property of glasses based on $\text{MnO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ may be of value in the preparation of thin glass targets for electron image tubes such as the Image Orthicon. According to McMillan, the glass film must be

approximately 0.002 inch thick and its volume resistivity should be 10^{11} to 10^{12} ohm-cm at room temperature. Glasses containing high proportions of alkali ions which have the correct resistivity suffer from the disadvantage of polarization since the current-carriers through the film are alkali ions. This apparently limits the operating life of a tube. The substitution by a semiconducting glass will thus be advantageous.

Both the $\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2^{24}$ and the vanadate glasses are transparent in the infrared, but are opaque in the visible. McMillan has suggested that these glasses may be useful in infrared signalling and infrared detection devices.²⁴ Because of the absence of polarization and their low activation energies, semiconducting vanadate glasses have been suggested for use in surface junction detectors.²³ The ease of forming a glass into any physical shapes and the readiness of crystallization of glasses containing a large amount of transition metal oxides have led to the suggestion that they may be suitable substitutes for conventional sintered ceramic bodies with electronic conductivity.³³ The relatively large thermoelectric power and its small dependence on temperature suggest the possible use of such semiconducting glasses as temperature sensors.

IX. SUMMARY

Although most of the commonly encountered glasses such as soda-lime glass are ionic conductors, it is theoretically possible to prepare oxide glasses which are electronic conductors. A general principle for the preparation of such semiconducting glasses is described. The various methods to prove electronic conduction in some of these glasses are discussed. A critical review of the electrical conductivity and thermoelectric power of known semiconducting glasses, in particular those in the V_2O_5 - P_2O_5 -RO systems, is presented. Some of the more important factors governing conduction are discussed. Finally, a summary is given of the possible applications of this new type of semiconductors.

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Table I. Summary of Published Work on Semiconducting Oxide Glasses. a) electrical conductivity; b) thermoelectric power; c) optical properties; d) magnetic susceptibility; e) thermal expansion.

System	Properties Studied	Temp. Range °C	Ref
V ₂ O ₅ .P ₂ O ₅	a	25-200	15
	a	40	16
	a,b,c	25-200	17
	a,b	25-250	18,19
V ₂ O ₅ .P ₂ O ₅ .Na ₂ O	d	25	20
	a	25-200	15
V ₂ O ₅ .P ₂ O ₅ .BaO	a	40	16
	a	25-200	15
	a,b	25-250	19
V ₂ O ₅ .P ₂ O ₅ .Na ₂ O.BaO	a,e	25-200	21
V ₂ O ₅ .P ₂ O ₅ .Na ₂ O.BaO	a	25-200	15
V ₂ O ₅ .P ₂ O ₅ .RO [*]	a	40	22
V ₂ O ₅ .P ₂ O ₅ .RO ^{**}	a,c	40	23
V ₂ O ₅ .P ₂ O ₅ .RO ^{***}	a,b,c	25-200	17
V ₂ O ₅ .BaO	a,c,e	25-200	21
V ₂ O ₅ .TeO ₂	a,c	25-200	21
V ₂ O ₅ .WO ₃ .K ₂ O	a,b	25-250	19
V ₂ O ₅ .GeO ₂ .BaO	a	25-100	12
V ₂ O ₅ .B ₂ O ₃ .CaO	a	25-300	12
V ₂ O ₅ .PbO.Fe ₂ O ₃	a	25-100	12
MnO.Al ₂ O ₃ .SiO ₂	a,c,e	25-500	24
CoO.Al ₂ O ₃ .SiO ₂	a,c,e	25-500	24
FeO.Al ₂ O ₃ .SiO ₂	a,c,e	25-500	24
CoO.P ₂ O ₅	a	50-400	12
Fe ₃ O ₄ .P ₂ O ₅ .CaO	a	50-400	12
MnO.B ₂ O ₃	a	25-300	12
CoO.B ₂ O ₃ .CaO	a	25-350	12
Fe ₃ O ₄ .B ₂ O ₃ .CaO	a	25-350	12
TiO ₂ .B ₂ O ₃ .BaO	a	25-250	12

(Table I-continued)

System	Properties	Temp. Range °C	Ref.
$\text{Fe}_2\text{O}_3.\text{SiO}_2.\text{B}_2\text{O}_3.$ $\text{Al}_2\text{O}_3.\text{CaO}$	a	150-300	25
$\text{Fe}_2\text{O}_3.\text{B}_2\text{O}_3.\text{SiO}_2.$ $\text{Al}_2\text{O}_3.\text{CaO}.\text{Na}_2\text{O}$	a	100-450	26
$\text{Fe}_3\text{O}_4.\text{Co}_3\text{O}_4.\text{MnO}.\text{RO}^{\dagger}$	a	50-600	27
$\text{Fe}_2\text{O}_3.\text{SiO}_2.\text{Na}_2\text{O}.\text{PbO}$	a	25-250	28

RO^* = Li, Na, K, Rb, Cs, Be, Ca, Sr, Ba, Zn, Cd, Pb, Ag,
and Tl singly

RO^{**} = Li, Na, K, Ba, Cd, and Pb singly

RO^{***} = Li, Be, Mg, Ca, Sr, Zn, Cd, Pb, Cu, Ag, Fe, Co,
Bi and Sb singly

RO^+ = Na, Mg, Al, B and Si mixtures.

Table II. Comparison of the activation energies for conduction for semiconducting glasses (E^*) and that for the corresponding glasses without the transition metal oxide (E) 12

No.	Composition (mole %)	E^* (kcal/mole)	E' (kcal/mole)
1	20Ba0.60GeO ₂ .20V ₂ O ₅	12.5	38.0
2	31Ca0.61B ₂ O ₃ .8Fe ₃ O ₄	15.7	40.0
3	30Ca0.60B ₂ O ₃ .10CoO	24.0	40.0

FIGURE CAPTIONS

- Figure 1. Electrical conductivity of V_2O_5 (semiconductor) and PbO (ionic conductor) on melting.⁶
- Figure 2. Electrical resistivity of silicate and borate glasses of higher sodium content compared with that of fused silica of lower sodium content.
- Figure 3. Time effects of 200-Volt DC on the electrical resistance of ionically conducting and semi-conducting glasses.¹²
- Figure 4. Apparatus for e.m.f. measurement when a glass is used as a solid electrolyte.¹² Only one of the identical two halves is shown.
- Figure 5. Effects of approximately hydrostatic pressure on the electrical resistivity of semiconducting vanadate glasses.
- Figure 6. Relation between resistivity and temperature for (1) polycrystalline V_2O_5 ; and glasses: (2) 83.0 V_2O_5 -10 P_2O_5 -6.5 Na_2O ; (3) 80 V_2O_5 -20 P_2O_5 ; (4) 75 V_2O_5 -20 P_2O_5 -5 BaO ; (5) 50.8 V_2O_5 -24.4 P_2O_5 -13.9 BaO -10.8 Na_2O . Composition in mole %.¹⁵
- Figure 7. Relation between resistivity and temperature for some semiconducting glasses.¹² (1) 50 CoO -50 P_2O_5 ; (2) 31 CaO -61 B_2O_3 -8 Fe_3O_4 ; (3) 20 BaO -60 GeO_2 -20 V_2O_5 . Composition in mole %.
- Figure 8. Relation between resistivity at 25°C and composition for glasses of the system V_2O_5 - P_2O_5 . Single crystal value from Boros³⁹; results of glasses from Grechanik et al.¹⁷ and Stanworth.¹⁵
- Figure 9. Resistivity-temperature relation for glasses of the system CaO -2 B_2O_3 containing iron oxide as function of Fe^{2+}/Fe^{3+} ratio.⁹

- Figure 10. Log resistivity at room remperature as a function of V_2O_5/P_2O_5 ratio.
- (1) Glasses from $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-BaO$ from results of Ioffe (19);
 - (2) Glasses from $V_2O_5-P_2O_5-BaO$ and $V_2O_5-P_2O_5-BaO-NaO$ from results of Baynton et al. (15); \bullet , $V_2O_5-P_2O_5-BaO$ (23); Δ , $V_2O_5-P_2O_5-CdO^{23}$
- Figure 11. Relation between resistivity and V^{4+}/V_{Total} for glasses of the system $V_2O_5.P_2O_5.BaO$ according to Munakata. (16)
- Figure 12. Variation of thermoelectric power with V^{4+} content in a $V_2O_5-P_2O_5$ glass. (18)
- Figure 13. Variation of thermoelectric power with metal oxides for $V_2O_5.P_2O_5.RO$ glasses with the P_2O_5 content constant at 20 mole %. Dashed curves are results of Grechanik, et al. (17), and other points are those of Mackenzie (9).
- Figure 14. Variation of the thermoelectric power of vanadate glasses with temperature. Lead, alumel and chromel refers to the reference metal from which the thermo e.m.f. was obtained.

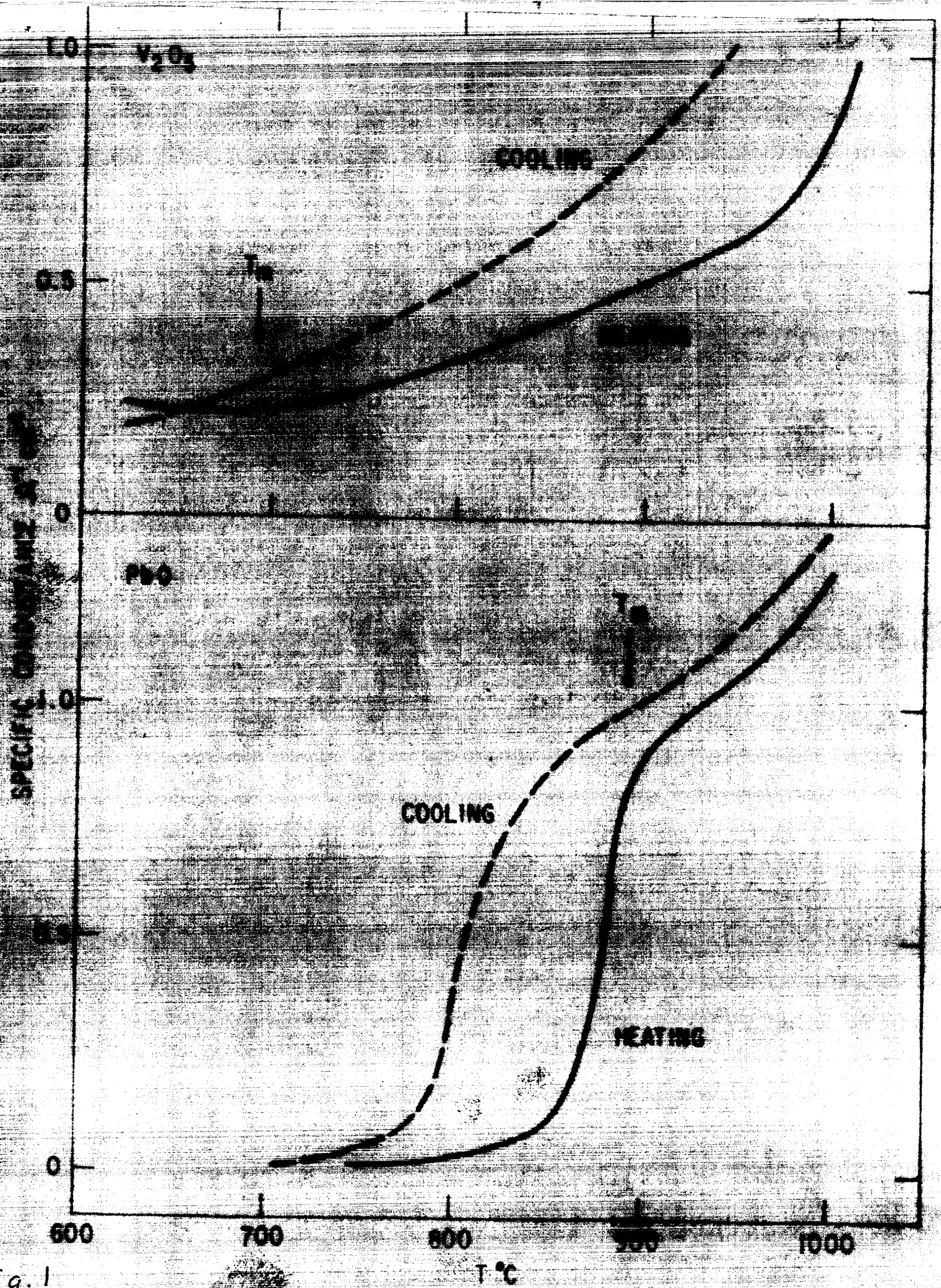


Fig. 1

LOG RESISTIVITY (OHM-CM)

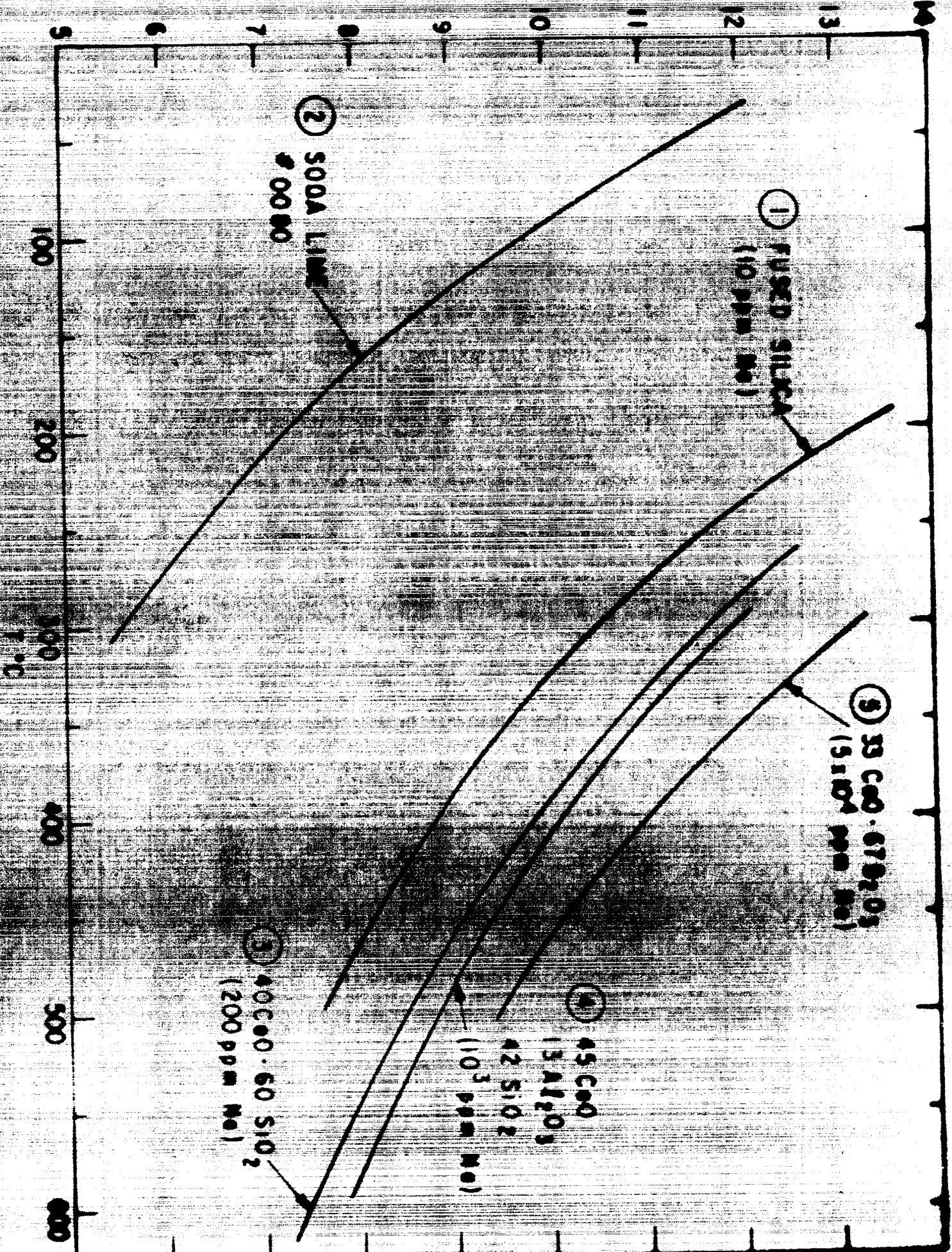


Fig. 2

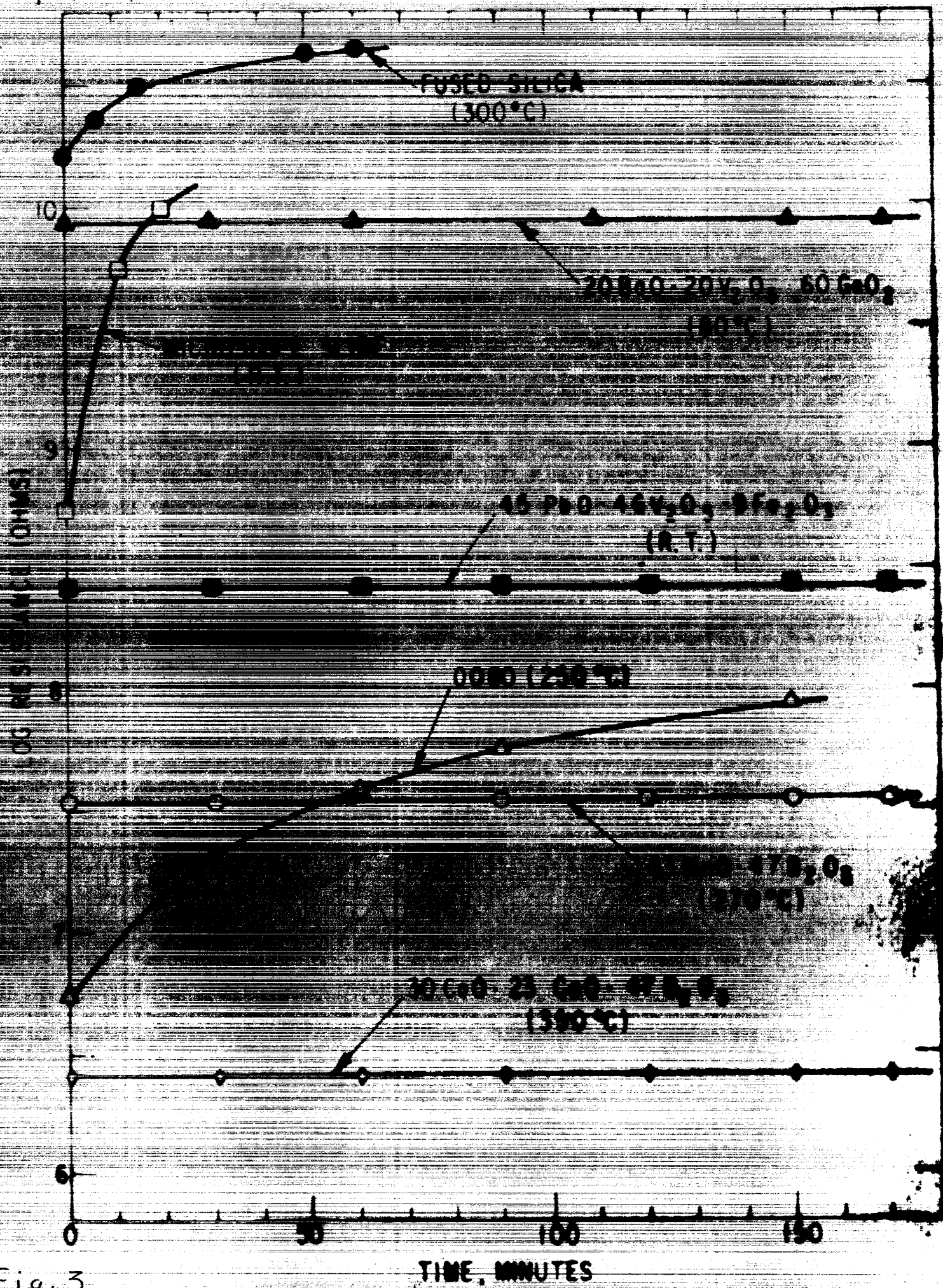


Fig. 3

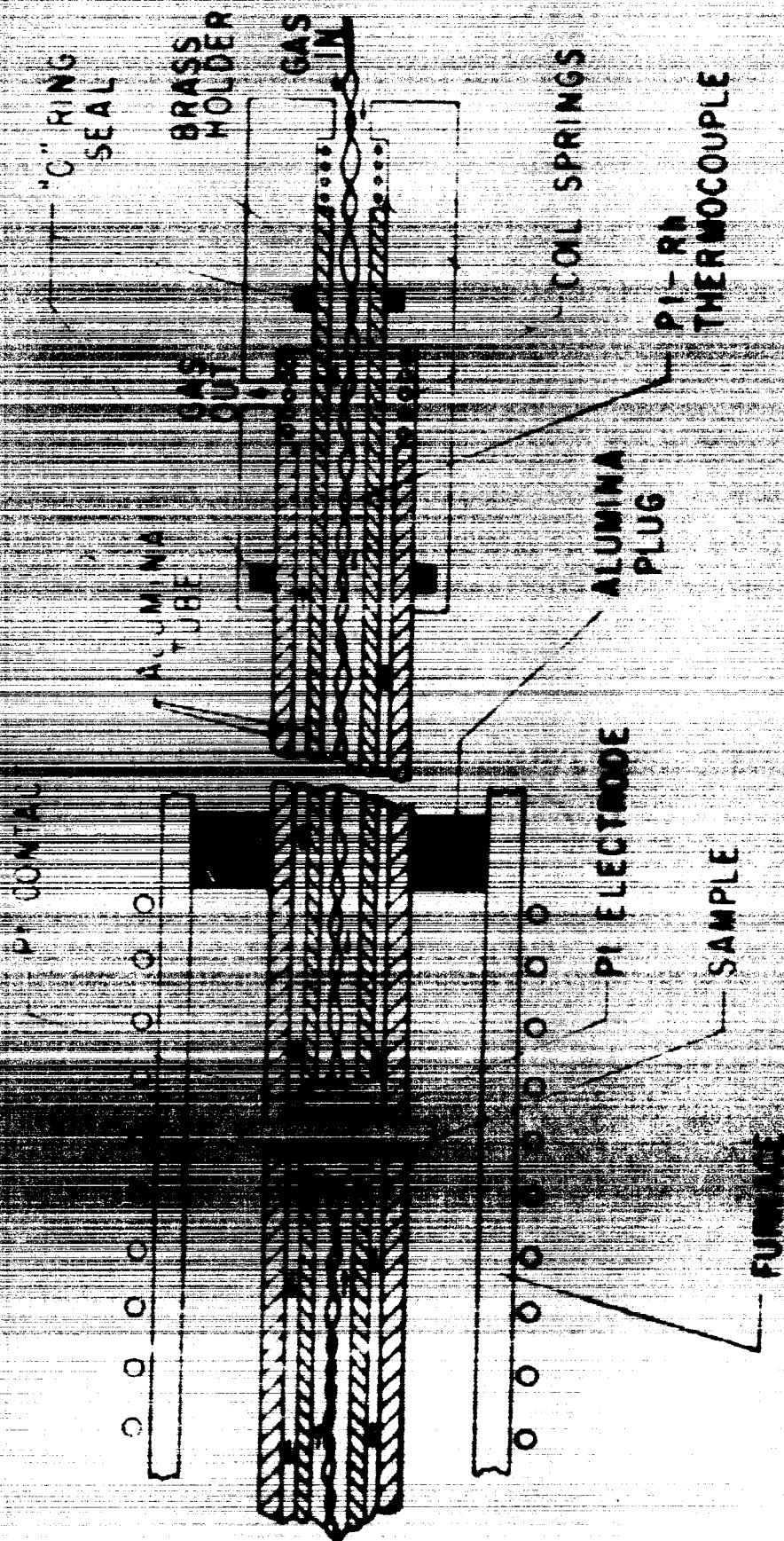


Fig. 4

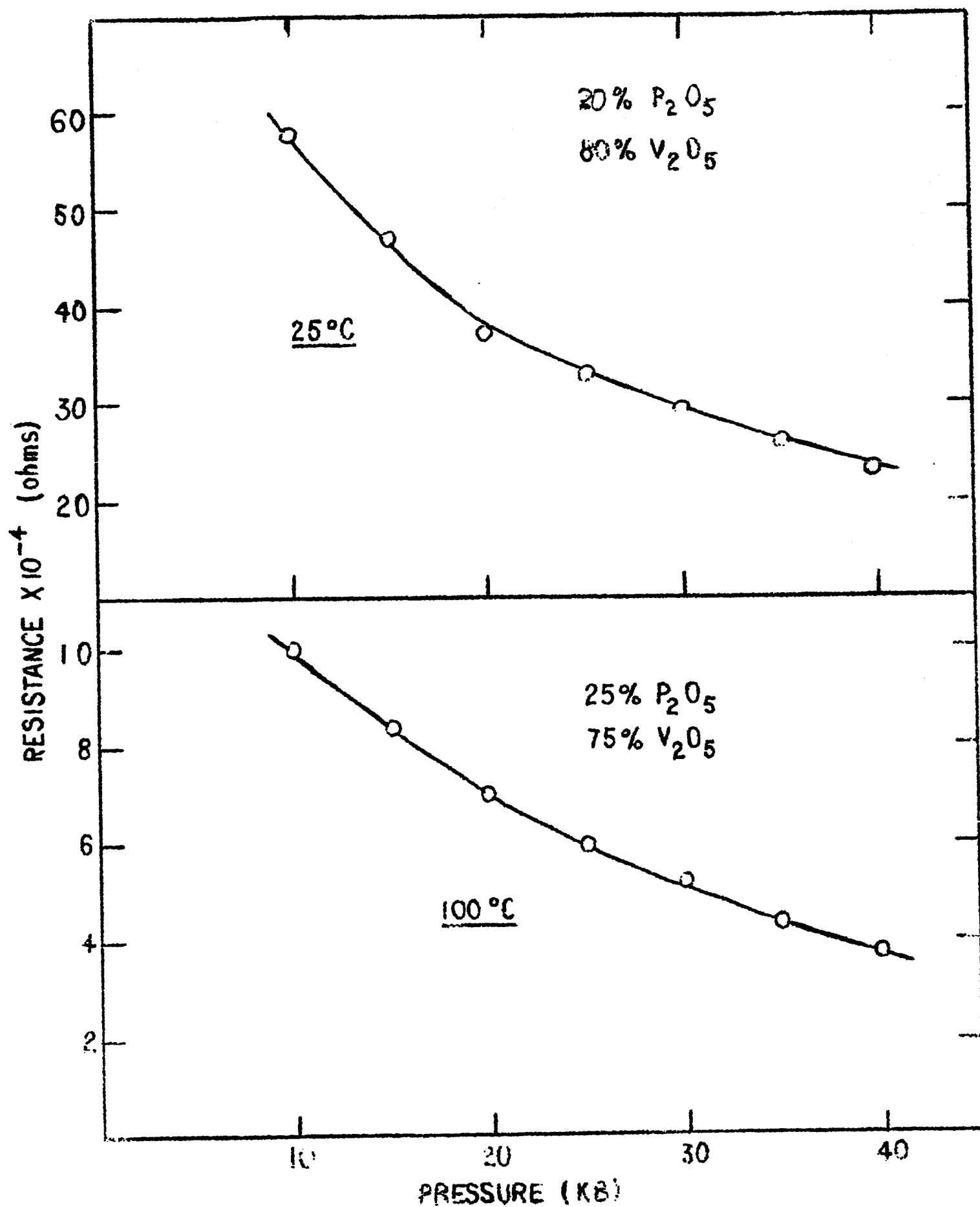


Fig. 5

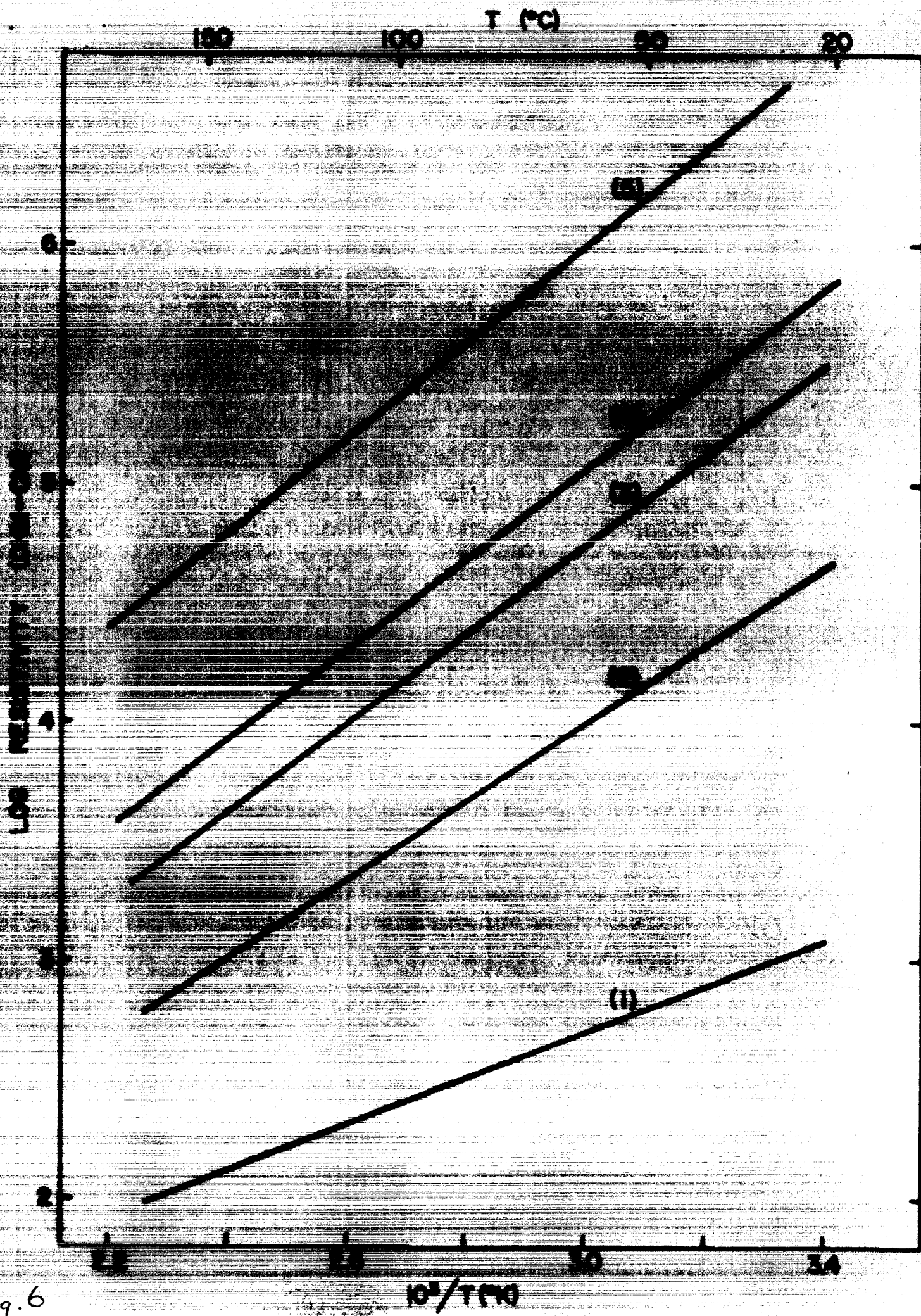


Fig. 6

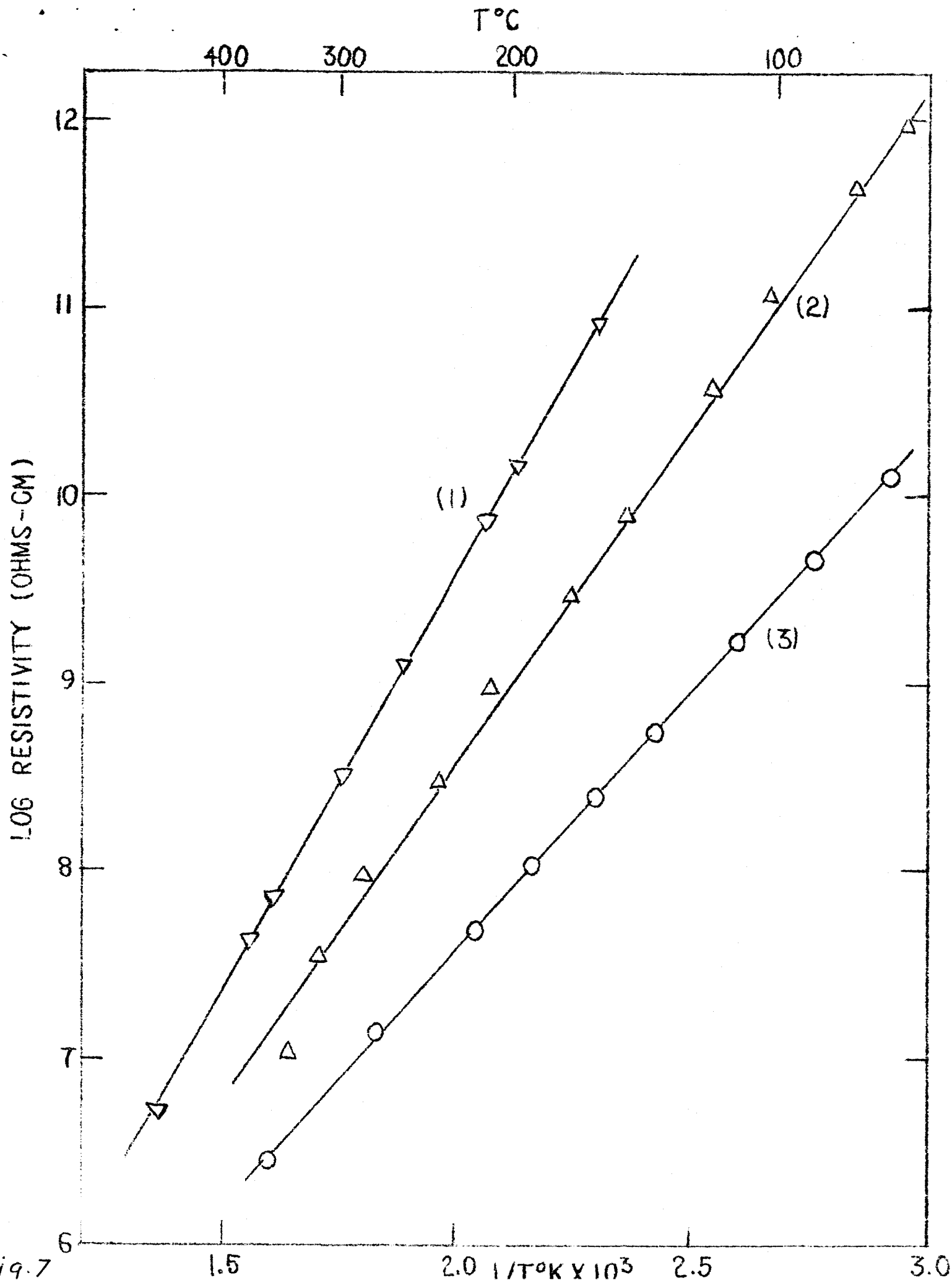


Fig. 7

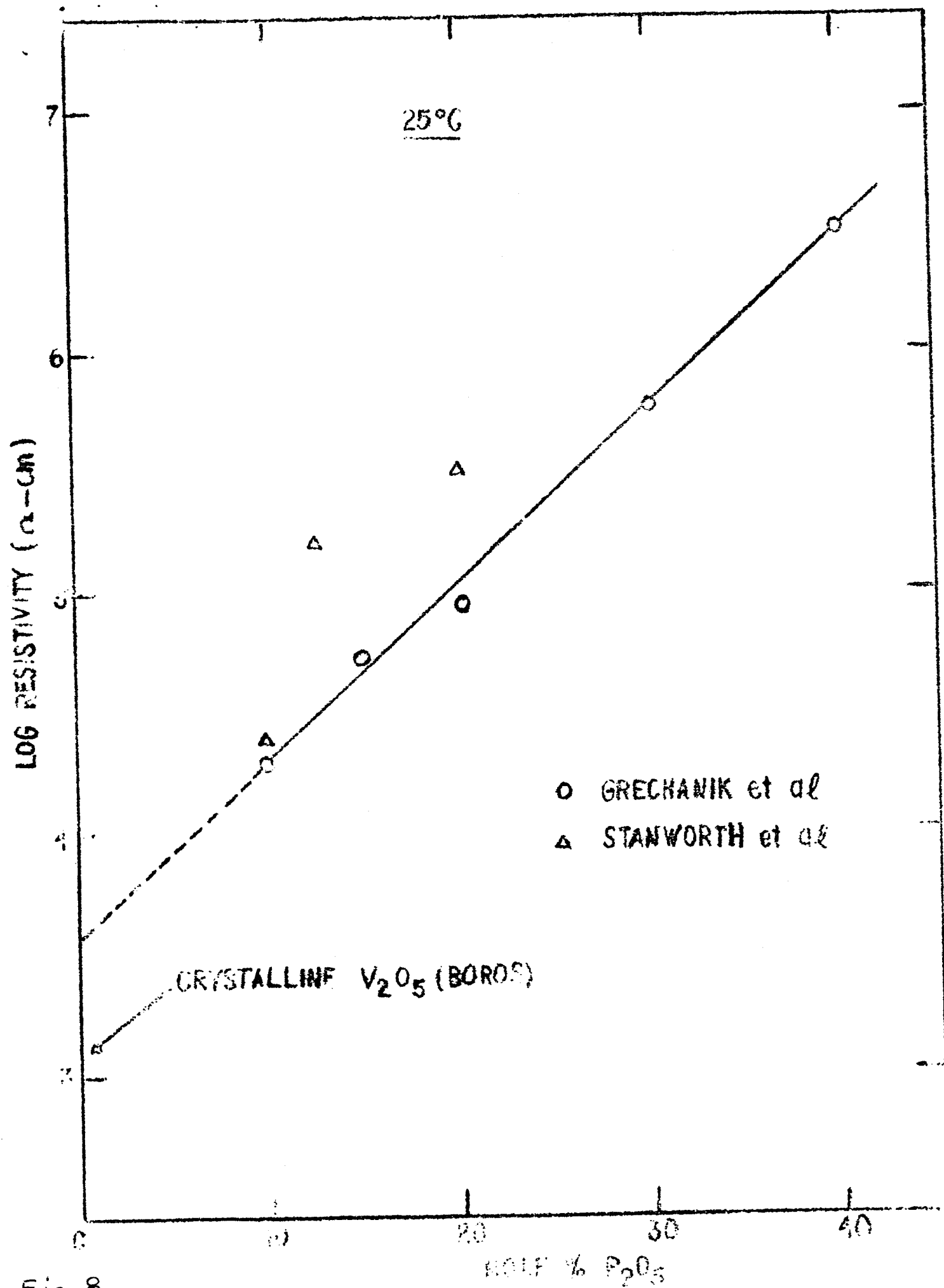


Fig. 8

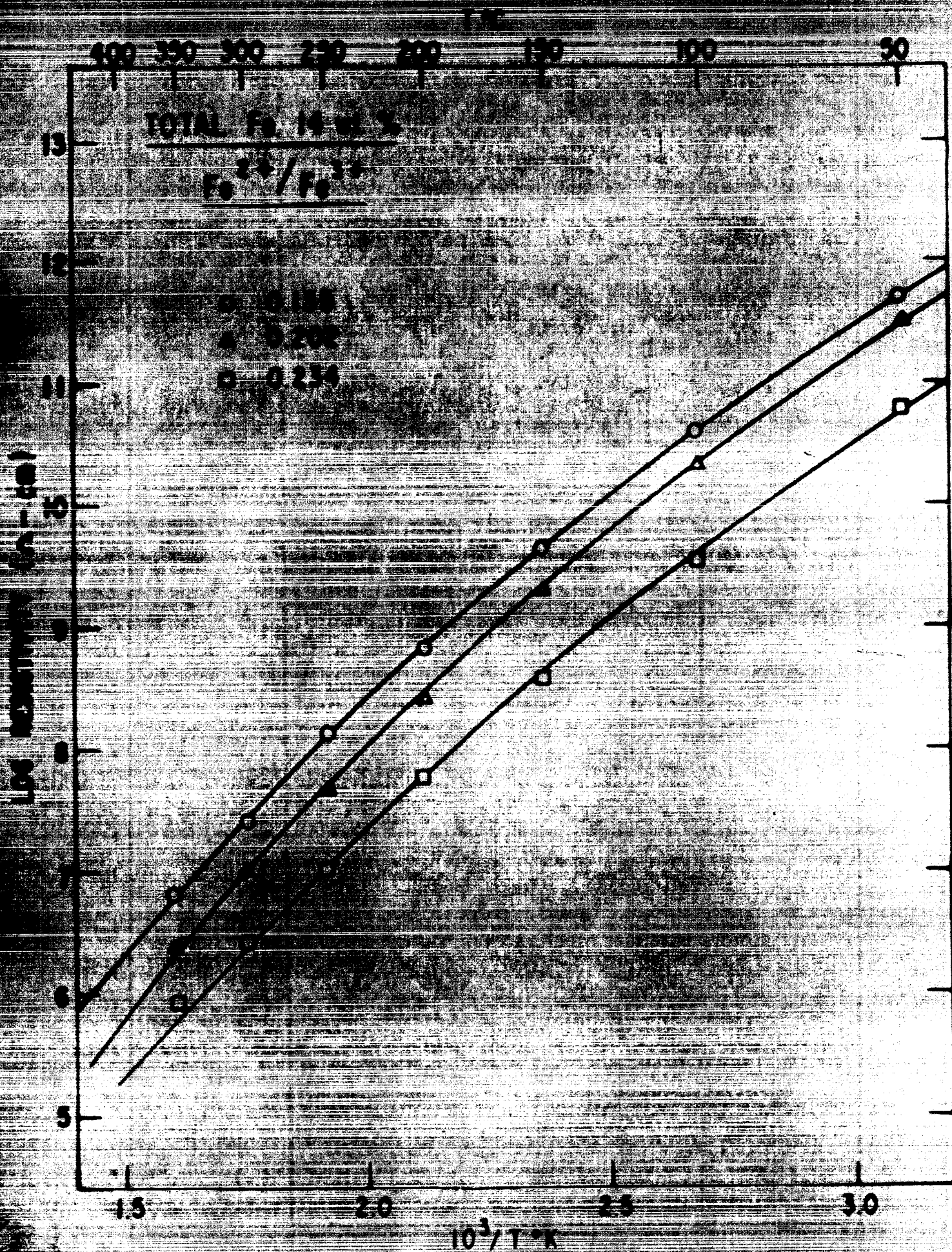


Fig. 9

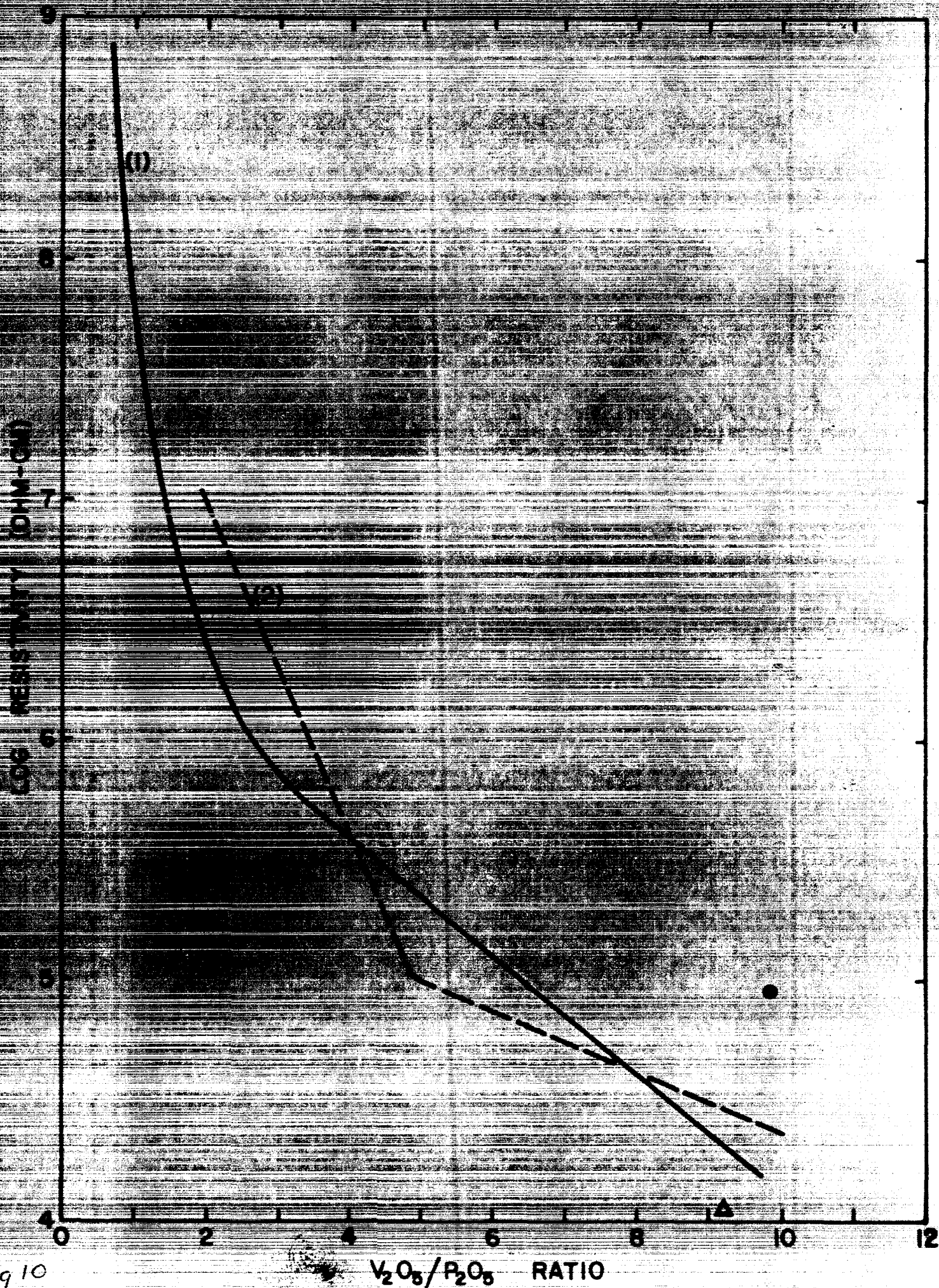


Fig 10

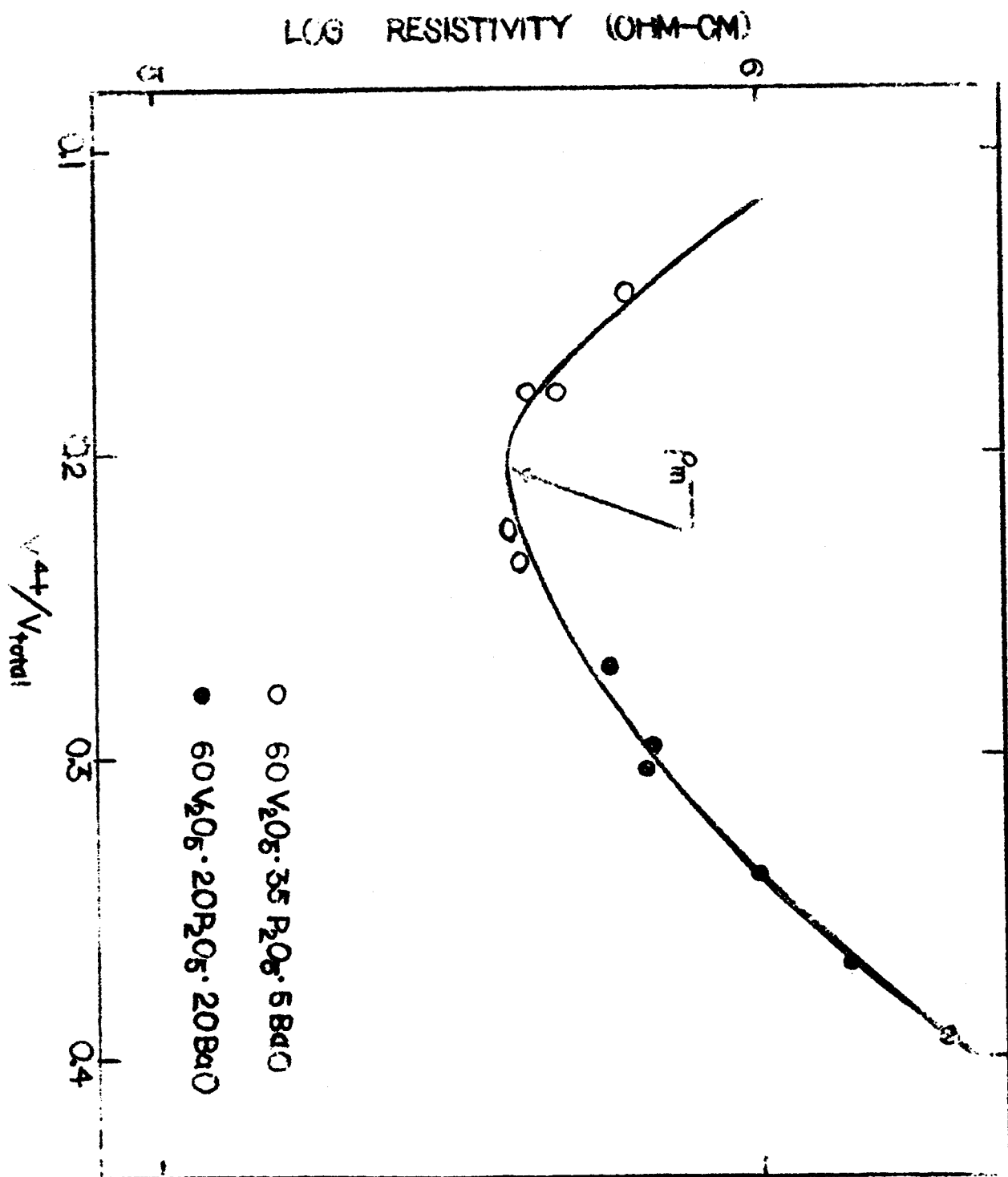


Fig. 11

KITAIGORODSKII et al (1961)

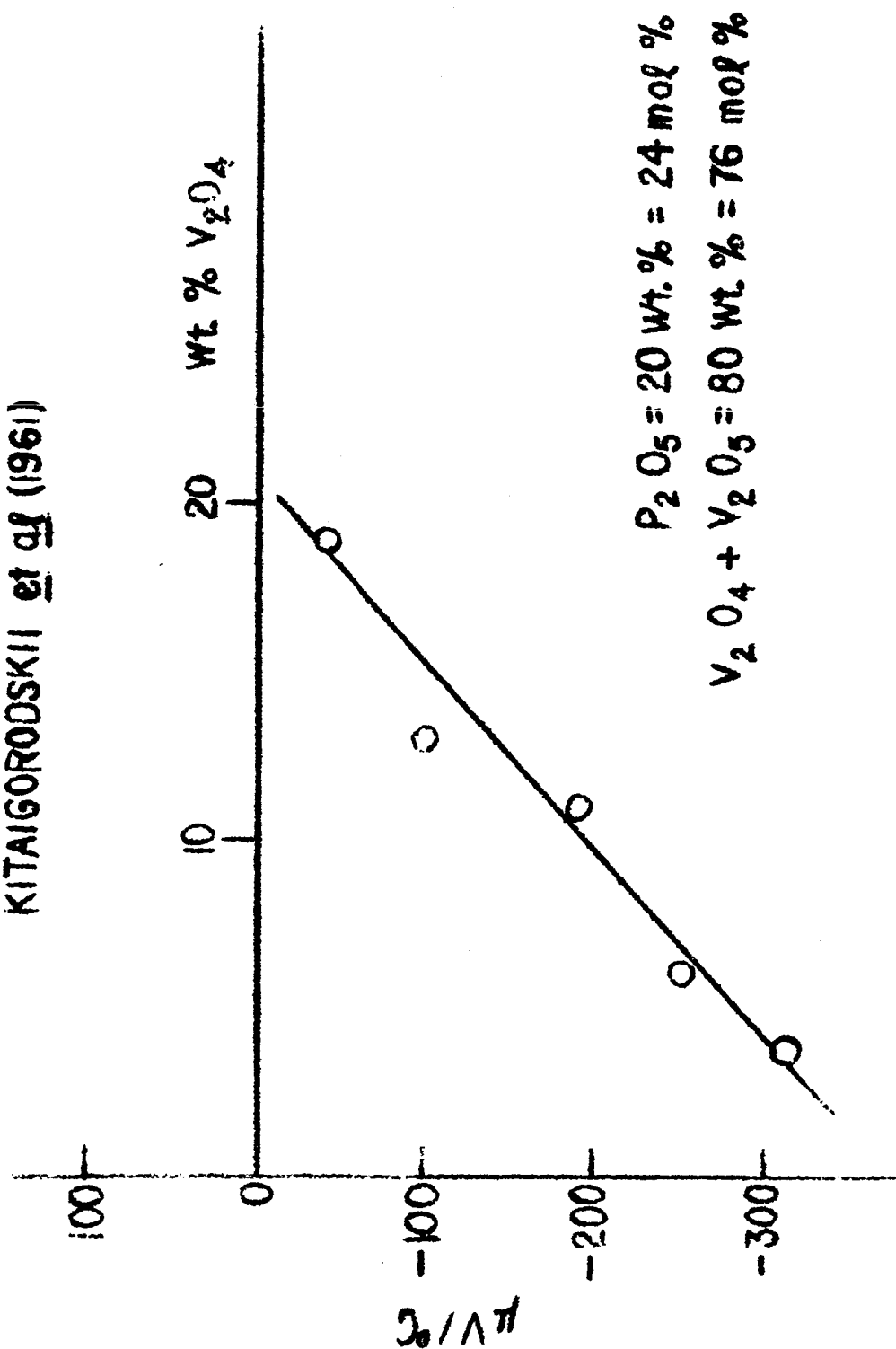


Fig. 12

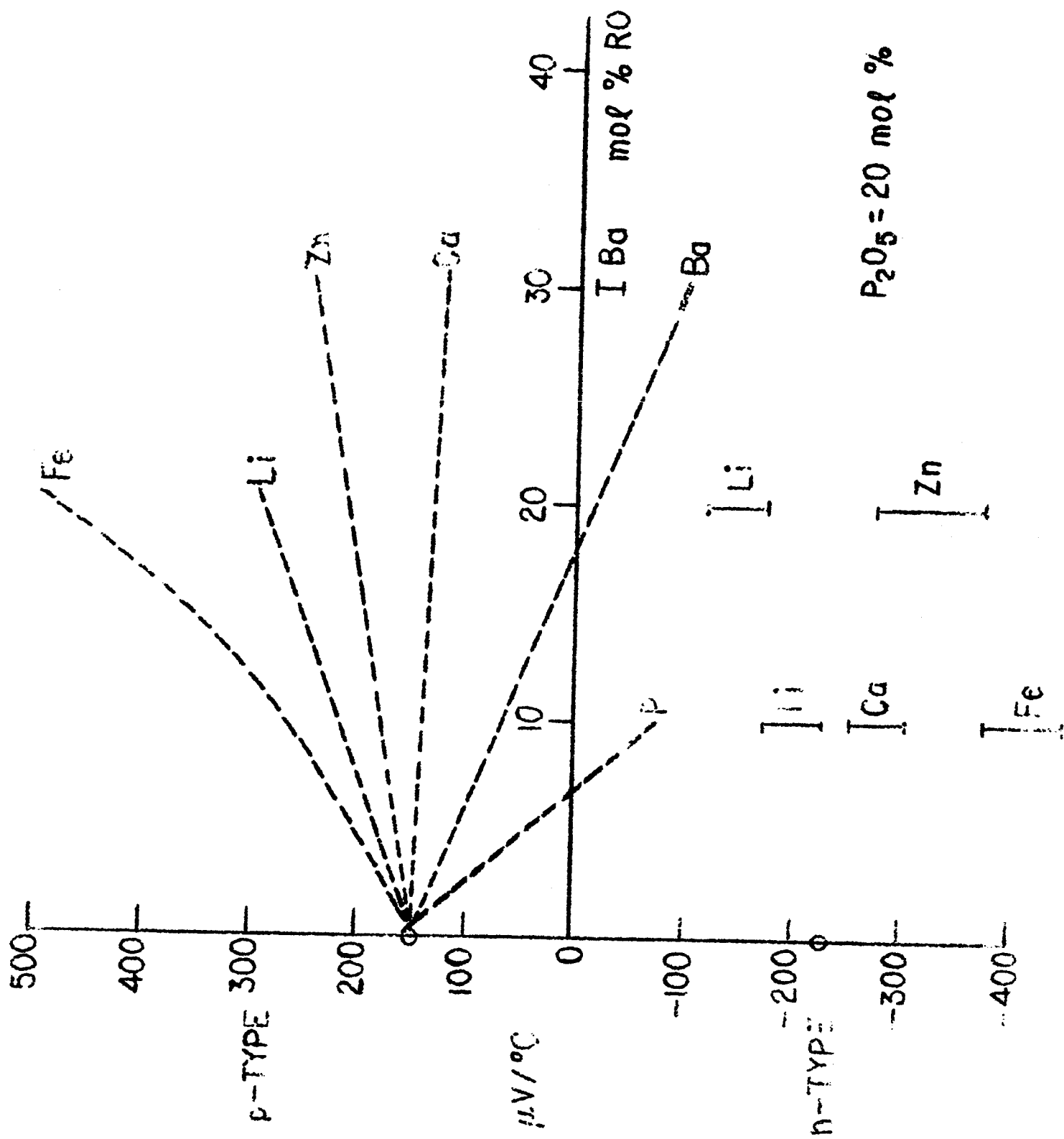


Fig. 13

Fig. 14

W/V

